

Electrochemiluminescence (ECL) of Ru(bpy)₃²⁺ in the Presence of Tripropylamine : Effects of Additives on the ECL Reaction

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In the last two decades, luminescence techniques have found widespread use in analytical chemistry, especially where sensitivity is of primary concern. Among these techniques, electrochemiluminescence or electrochemically generated chemiluminescence (ECL) offers some advantages over chemiluminescence or bioluminescence. For example, since ECL reactions are readily controllable electrochemically by controlling electrode potential or current to oxidize or reduce ECL-active species at electrode surfaces.

Ru(bpy)₃²⁺ and its derivatives are well-known by their stable ECL reactions in aqueous solutions in the presence of certain coreactant such as tripropylamine. A large number of researches have been carried out to enhance the ECL intensity of Ru(bpy)₃²⁺ complexes. It has been shown that the ECL intensity is strongly dependent on coreactants and their concentration and solution pH. Recently, halogen ions¹⁾ and nonionic surfactants²⁾ were reported to enhance the ECL intensity of Ru(bpy)₃²⁺ complex in the presence of tripropylamine.

In this study, significant enhancement in the ECL intensity was observed by adding sodium azide to an ECL solution containing Ru(bpy)₃²⁺ and tripropylamine. Furthermore, the ECL response increased at a more negative potential. It was also observed that the ECL-potential curves showed two peaks. The magnitudes of the both ECL response peaks were dependent on the concentration of sodium azide. The ECL intensities increased with increasing sodium azide concentration initially. However after passing through the maxima, the intensities decreased with further addition of sodium azide. The concentration of sodium azide at which the ECL intensities showed the maxima was dependent on tripropylamine concentration, being higher at a higher tripropylamine concentration. It was also shown that addition of sodium azide to an ECL solution affected electrochemical oxidation of tripropylamine at Pt electrode surfaces. In the presence of sodium azide, oxidation potential of tripropylamine shifted in the negative direction. We expected in the presence of sodium azide, formation of surface oxide layer on Pt electrodes would be inhibited and, at Pt electrodes without surface oxide layers, oxidation of tripropylamine might proceed faster than Pt electrodes covered with surface oxide layers, leading to the enhanced ECL response at a more negative potential in the

presence of sodium azide. It may be also possible that azide ion promotes the formation of tripropylamine radical, which is an essential reducing agent in the Ru(bpy)₃²⁺-tripropylamine ECL system, by extracting a proton from tripropylamine cation radical to yield tripropylamine radical, resulting in the enhanced ECL response.

We also observed that addition of surfactants such as Tween 20 and Triton X-100 enhanced the ECL response of Ru(bpy)₃²⁺ in the presence of tripropylamine, although the ECL-potential curves were highly complex.

Mechanisms for the enhancement of the ECL responses in the presence of the additives will be present in more detail.

REFERENCES

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